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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] In the lamination film laminated in this order, respectively, a polyamide resin (X) layer, an adhesive resin (Y) layer, and a thermoplastics (Z) layer [polyamide resin (X)] When it is the range of relative viscosity 3.0-6.0, the number of end carboxyl groups is used as (A) and (1g of mueq / resin) and the number of end amino groups is used as (B) and (1g of mueq / resin), an end group -- quantity -- a difference -- (-- C --) -- (-- B --) -- (-- A --) -- -- ten -- more than -- it is -- and -- water extraction -- quantity -- two -- weight % -- less than -- it is -- polyamide resin -- from -- constituting -- having -- becoming -- Thermoplastics (Z) is a lamination film which it comes to consist of the melting point thermoplastics of the range which are 100 degrees C - 170 degrees C, and is characterized by the ratios of the thickness of the above-mentioned lamination film being the (X) layer 90 - 10% and the (Y) layer 1 - 50% and 10 to 90% of the (Z) layer.

[Claim 2] The lamination film according to claim 1 with which 0.001-1 weight part combination of the antioxidant is carried out for a polyamide resin (X) layer to a polyamide resin (X) 100 weight part.

[Claim 3] The lamination film according to claim 2 whose antioxidant is a hindered phenolic antioxidant.

[Claim 4] an antioxidant -- and/or (N and N'-HEKISA methylene screw (3, 5-G t-butyl 4-hydroxy hydronalium thinner MAMIDO)), it is pentaerythrityl tetrakis {3-(3, 5-G t-butyl 4-hydroxyphenyl) propionate} -- A lamination film according to claim 2.

[Claim 5] A lamination film given in any 1 clause of Claim 1 or Claim 4 whose polyamide resin is polyamide 6 / [polyamide 6 and/or] 66 copolymer.

[Claim 6] A lamination film given in any 1 clause of Claim 1 or Claim 5 which a thermoplastics (Z) layer becomes from either or these mixtures of polypropylene, polyethylene, and a polypropylene copolymer.

[Claim 7] A lamination film given in any 1 clause of Claim 1 or Claim 6 whose intensity maintenance rate after [30 minutes] carrying out pneumaticity retorting a lamination film is 60% or more at 130 degrees C about this.

[Claim 8] In the becoming packing object, a polyamide resin (X) layer, an adhesive resin (Y) layer, and a thermoplastics (Z) layer from the lamination film laminated in this order [polyamide resin (X)] When it is the range of relative viscosity 3.0-6.0, the number of end carboxyl groups is used as (A) and (1g of mueq / resin) and the number of end amino groups is used as (B) and (1g of mueq / resin), an end group -- quantity -- a difference -- (-- C --) -- (-- B --) - (-- A --) --} ten -- more than -- it is -- and -- water extraction -- quantity -- two -- weight % -- less than -- it is -- polyamide resin -- from -- constituting -- having -- becoming -- Thermoplastics (Z) is a packing object made from a lamination film which the melting point consists of thermoplastics of the range which are 100 degrees C - 170 degrees C, and is characterized by coming to make a thermoplastics (Z) layer into an innermost layer.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a lamination film and a packing object. Furthermore, it is related with a lamination film suitable for the packing object manufacture for retorts which consists of a lamination film which made polyamide resin the main composition layers in detail, and the packing object which consists of this lamination film.

[0002]

[Description of the Prior Art] Since polyamide resin is excellent in intensity, pliability, transparency, heat resistance, chemical resistance, gas barrier nature, etc., the cast and the film are widely used for packing uses and container uses, such as food packing material and a packaging medium for Medical Science Division. After storing and packing food, for example like a retort pouch in the packaging medium used for a food use, it is the purpose which sterilizes botulinus bacillus etc., Germicidal treatment may be carried out under the conditions which made steam and air of the temperature range of 110-145 degrees C intermingled (hereafter, this germicidal treatment is called "pneumaticity retorting" and the container used in this case is called "retort container"). With the film which consists of polyamide resin known conventionally, after carrying out the above-mentioned pneumaticity retorting, the intensity and shock nature of the packaging medium fell, and the pinhole arose and there was a problem of a content being revealed.

[0003] Various trials are made for the purpose of improving the quality after pneumaticity retorting of the film which consists of these polyamide resin. For example, although the technique of denaturing the end carboxyl group of polyamide resin with fatty series mono-

amine was indicated by the patent No. 3008445 gazette, the strength reduction prevention effect of the packaging medium after pneumaticity retorting was inadequate for it. Moreover, it is in JP,H7-138472,A, JP,H7-268209,A, and the patent No. 2917401 gazette, Although the technique of blending an antioxidant with polyamide resin was indicated for strength reduction prevention of the packaging medium after pneumaticity retorting, it could not be said that the strength reduction prevention effect of the packaging medium after pneumaticity retorting was still enough.

[0004]

[Problem(s) to be Solved by the Invention] This invention comes to be wholeheartedly completed as a result of examination that a lamination film suitable for retort container manufacture and the packing object which consists of this lamination film should be offered in view of this situation. a lamination film suitable as packaging media, such as food with high seal intensity intensity does not deteriorate easily even if it carries out (1) pneumaticity retorting, and the purpose of this invention excels [food] in heat-sealing nature and by which pneumaticity retorting is carried out, and (2) -- it is offering the packing object which consists of this lamination film.

[0005]

[Means for Solving the Problem] In the lamination film which laminates a polyamide resin (X) layer, an adhesive resin (Y) layer, and a thermoplastics (Z) layer in this order in the 1st invention, respectively in order to solve the above-mentioned technical problem When polyamide resin (X) is the range of relative viscosity 3.0-6.0, the number of end carboxyl groups is used as (A) and (1g of mueq / resin) and the number of end amino groups is used as (B) and (1g of mueq / resin), an end group -- quantity -- a difference -- (-- C --) -- {-- (-- B --) - (-- A --) --} -- ten -- more than -- it is -- and -- water extraction -- quantity -- two -- weight % -- less than -- it is -- polyamide resin -- from -- constituting -- having -- becoming -- It comes to consist of thermoplastics (Z) thermoplastics of the range whose melting points are 100 degrees C - 170 degrees C, and the ratio of the thickness of the above-mentioned lamination film offers the lamination film characterized by being the (X) layer 90 - 10% and the (Y) layer 1 - 50% and 10 to 90% of the (Z) layer.

[0006] Moreover, in the 2nd invention, a polyamide resin (X) layer, an adhesive resin (Y) layer, and a thermoplastics (Z) layer are set on the packing object which consists of a lamination film laminated in this order. When polyamide resin (X) is the range of relative viscosity 3.0-6.0, the number of end carboxyl groups is used as (A) and (1g of mueq / resin) and the number of end amino groups is used as (B) and (1g of mueq / resin), an end group -- quantity -- a difference -- (-- C --) -- {-- (-- B --) - (-- A --) --} -- ten -- more than -- it is -- and -- water extraction -- quantity -- two -- weight % -- less than -- it is -- polyamide resin -- from -- constituting -- having -- becoming -- The packing object made from a lamination film characterized by the melting point

consisting of thermoplastics of the range which are 100 degrees C - 170 degrees C, and coming to make thermoplastics (Z) into an innermost layer in a thermoplastics (Z) layer is offered.

[0007]

[Embodiment of the Invention] It explains to details per this invention hereafter. It functions as polyamide resin (X) in this invention raising the gas barrier nature of a lamination film. Polyamide resin (X) is obtained by heavy condensation or copolymerization reactions, such as RAKUTAMU of three or more membered-rings, omega-amino acid which can be polymerized, or dibasic acid and Gia Min. Specifically as RAKUTAMU of three or more membered-rings, epsilon-caprolactam, ENANTORAKUTAMU, capryl, lauryl RAKUTAMU, alpha-pylori boss, alpha-PIPERIDON, etc. are mentioned. Specifically as omega-amino acid, 6-aminocaproic acid, 7-amino heptanoic acid, 9-amino nonanoic acid, 11-amino undecanoic acid, etc. are mentioned.

[0008] As dibasic acid, specifically Malonic acid, KOHAKU acid, glutaric acid, Adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, UNDE can dione acid, dodeca dione acid, trideca dione acid, TETORADE rudder-on acid, HEKISADE rudder-on acid, HEKISA decene dione acid, OKUTADE rudder-on acid, Aromatic series dicarboxylic acid, such as fatty series dicarboxylic acid, such as octadecene dione acid, EIKOSAN dione acid, ENKOSEN dione acid, DOKOSAN dione acid, 2 and 2, and 4-bird MECHIRU adipic acid, and terephthalic acid, isophthalic acid, phthalic acid, KISHIRI range carboxylic acid, is mentioned.

[0009] As Gia Min, specifically Ethylene diamine, trimethylene diamine, Tetramethylen JIAMIN, pentamethylene JIAMIN, HEKISAMECHI range amine, Heptamethylene JIAMIN, octa methylene JIAMIN, nonamethylene JIAMIN, Undecamethylene JIAMIN, dodeca methylene JIAMIN, 2, 2, 4 -(or 2, 4, 4)- Trimethylhexamethylene JIAMIN, cyclo HEKISANJ amine, ****- (4 and 4'-amino cyclohexyl) methane, meta-KISHIRI range amine, etc. are mentioned.

[0010] The copolymers (polyamide 6 / 66 copolymer) of Polly epsilon-caprolactam (polyamide 6), epsilon-caprolactam, adipic acid, and HEKISAMECHI range amine, these mixtures, etc. are desirable as polyamide resin (A).

[0011] It is indicated that it is effective in the patent No. 3008445 gazette to reduce the amount of end carboxyl groups in order for smallness to make strength reduction after pneumaticity retorting there be nothing, and it is effective also when there are both amounts of end amino groups and amounts [few] of end carboxyl groups. However, according to the experiment of this invention persons, when there are both amounts of end amino groups and amounts [few] of end carboxyl groups It turned out that the strength reduction of the film after pneumaticity retorting is large, and only when there were more amounts of end amino groups from the amount of end carboxyl groups than the specified quantity, it turned out that the strength reduction behind a retort becomes small and it becomes so good that the difference of the

amount of end groups is large.

[0012] In order to attain the purpose of this invention effectively according to the experiment of this invention persons an end -- a carboxyl group -- a number -- (-- A --) -- (-- mu -- eq -- /-- resin -- one -- g --) -- carrying out -- an end -- an amino group -- a number -- (-- B --) -- (-- mu -- eq -- /-- resin -- one -- g --) -- carrying out -- the time -- an end group -- quantity -- a difference -- (-- C --) -- {(-- C --) -- = -- (-- B --) - (-- A --) --} -- ten -- more than -- it is necessary to carry out -- things -- I understand . The difference (C) of the amount of end groups becomes [the film strength reduction after pneumaticity retorting] large and is not desirable at less than ten. As for the difference (C) of the amount of end groups, 15 or more are more desirable, and 20 or more are the most desirable.

[0013] While reducing the amount of end carboxyl groups by comparatively little Gia Min when manufacturing polyamide resin and denaturing by Gia Min in order to enlarge the difference of the amount of end groups in this way, the amount of end amino groups can be increased. When denaturing polyamide resin with mono-amine, the amount of end carboxyl groups can be reduced, but since it is necessary to increase the amount of addition of mono-amine since the amount of end amino groups does not increase, and heavy condensation reaction speed falls as a result, it is not desirable. In order to enlarge as in this invention for the difference of the amount of end groups, denaturing using Gia Min is industrially desirable.

[0014] [the difference of the amount of end groups of polyamide resin (X)] in order to make it be that this invention prescribes What is necessary is to perform a heavy condensation reaction under Gia Min's coexistence, when using RAKUTAMU of three or more membered-rings, and omega-amino acid as materials, to make Gia Min into an excessive quantity and just to perform a heavy condensation reaction, when using dibasic acid and Gia Min as materials. As Gia Min for denaturation, in above any case, the Gia Min same in the materials for the above-mentioned polyamide resin manufacture can be used, and it is especially desirable. [of HEKISAMECHI range amine]

[0015] Polyamide resin (X) can be manufactured by the method known from the former which adopts decompression conditions as the end of a reaction. And Gia Min for denaturation can be added in arbitrary stages until it starts the heavy condensation reaction under decompression. 70 or less KPa of pressure of the end of a heavy condensation reaction is usually 50 or less KPa preferably. Moreover, the time of a decompression reaction is usually about 1 to 4 hours.

[0016] Measurement of the amount of end groups of polyamide resin (X) can be performed by the method known from the former which is indicated, for example in the "polymer analysis handbook" (edited by Japan Society for Analytical Chemistry). That is, the end amino group is measurable by dissolving polyamide resin in phenol and titrating with 0.01N chloride, and the end carboxyl group is measurable by dissolving polyamide resin in benzyl alcohol and titrating

with 0.01N caustic alkali of sodium. What is necessary is to be eluted and to make only a polyamide resin layer a fixed quantity by the above-mentioned method per [which was eluted] sample using a suitable solvent, in measuring the amount of end groups of the polyamide resin layer in a lamination film.

[0017] The relative viscosity of polyamide resin (X) is JIS. The value measured based on K6810 at the concentration in 98% sulfuric acid of 1% and the temperature of 25 degrees C is meant, and it is required to be 3.0-6.0. Since fusion viscosity is small, manufacture (film production) of a film becomes it difficult that relative viscosity is less than 3.0. Moreover, if relative viscosity exceeds 6.0, fusion mobility is inadequate and it is not desirable. As for the relative viscosity of polyamide resin, it is more desirable that it is 3.0-5.5. What is necessary is to be eluted and to make only a polyamide resin layer a fixed quantity by the above-mentioned method per [which was eluted] sample using a suitable solvent, in order to measure the relative viscosity of the polyamide resin layer in a lamination film.

[0018] In order to attain the purpose of this invention effectively, the amount of water extraction of polyamide resin (X) needs to be 2% or less. If the amount of water extraction exceeds 2%, the quantity of the gas which occurs at the time of film manufacture increases, and it becomes easy to come out of a die line or a fish eye, and is not desirable on film manufacture. 1.5% or less of the amount of water extraction is more desirable. Measurement of the amount of water extraction carries out boiling flowing-back extraction of 10g of the samples in 250ml of demineralized water for 6 hours, and after cooling the extraction liquid, it measures the carbon concentration C in a diluted solution (weight %) by a TOC analyzer (the Shimadzu make, TOC-500 type) after dilution with demineralized water 4 times. this carbon concentration C -- following type [of water extraction], i.e., amount, $=Cx4x(113/72) \times$ -- it is computable in be alike 250/10.

[0019] Strength reduction of the film after pneumaticity retorting can be made small by blending an antioxidant with polyamide resin (X). Although the antioxidant of ****, an amine system, a hindered phenol system, a phosphorus system, and a sulfur system can be used for an antioxidant, when it takes into consideration using it for a food use, a hindered phenolic antioxidant is desirable.

[0020] As a hindered phenolic antioxidant An N and N'-HEKISA methylene screw (3, 5-G t-butyl 4-hydroxy hydronalium thinner MAMIDO) or pentaerythrityl tetrakis [3-(3, 5-G t-butyl 4-hydroxyphenyl) propionate], and these mixtures are mentioned.

[0021] The amount of addition of an antioxidant has desirable 0.001 - 1 weight part to a polyamide resin (X) 100 weight part. When there are few amounts of addition than 0.001 weight part, there is no effect of making small strength reduction of the film after pneumaticity retorting. It becomes easy to exfoliate and is not desirable, when the amount of BURIDO out on the surface of a film increases, printing aptitude falls and it is made a lamination film, after

manufacturing a film, when more than 1 weight part. The amount of addition of an antioxidant has a more desirable 0.01 - 0.5 weight part, and its 0.01 - 0.25 weight part is the most desirable.

[0022] In polyamide resin (X), a filler with an average particle diameter of 10 micrometers or less can be blended, and when a polyamide resin layer is the outermost layer, the slide nature of a film can be improved. If the average particle diameter of a filler exceeds 10 micrometers, the light scattering effect of the filler itself becomes large, and the transparency of a film falls and is not desirable. In the case of an oriented film, 0.5-5 micrometers has more desirable average particle diameter, and when it is a non-oriented film, the average particle diameter of 1-10 micrometers is more desirable. The average particle diameter of a filler can be easily measured by the measuring method and electron microscope observation by the coulter counter method or the laser diffracting method.

[0023] The amount of addition of a filler with an average particle diameter of 10 micrometers or less has a desirable 0.001 - 1.0 weight part to a polyamide resin 100 weight part. When there are few amounts of addition than 0.001 weight part, there is no addition effect, if more than 1 weight part, the transparency of a film will fall, and neither is desirable. The amount of addition of a filler has a more desirable 0.01 - 0.6 weight part. As for the refractive index of a filler with an average particle diameter of 10 micrometers or less, it is desirable to resemble it of polyamide resin from a viewpoint of transparency. The refractive indices of a filler are 1.3-1.8 preferably, and are 1.4-1.7 more preferably.

[0024] As a filler with an average particle diameter of 10 micrometers or less, an inorganic compound, organic compounds, and these mixtures are mentioned. As an inorganic compound, zeolite, talc, kaolin, a vent night, The Mon Moliro night, calcium carbonate, carbonic acid zinc, straw SUTONAITO, silica, Various natural minerals and compounds, such as alumina, magnesium oxide, silicic acid calcium, sodium aluminate, aluminosilicic acid sodium, silicic acid magnesium, a glass balloon, a zinc oxide, and a hydrotalcite, are mentioned. Kaolin, talc, zeolite, silica, etc. are desirable and zeolite and its silica are especially the most desirable. Although the granular thing of various polymer, fine powder, a pulverization article, etc. are mentioned as an organic compound, bridge construction poly methyl methacrylate (bridge construction PMMA) is mentioned preferably.

[0025] When fabricating an oriented film, as for a filler with an average particle diameter of 10 micrometers or less, it is desirable to carry out the surface treatment of the filler by the Silang coupling agent. When a surface treatment was not carried out and extension fabrication is carried out, the border plane on polyamide resin (X) and the surface of a filler may separate, a void may occur in a border plane, and the transparency of a film may fall.

[0026] As a Silang coupling agent, specifically Trimethylmethoxysilane, vinyltriethoxysilane, gamma-chloropropyltrimethoxysilane, gamma-aminopropyl triethoxysilane, N-(beta-aminoethyl)-

gamma-aminopropyl trimethoxysilane, etc. are mentioned and vinyltriethoxysilane, gamma-aminopropyl triethoxysilane, etc. are mentioned. the amount of addition of the Silang coupling agent receives a filler 100 weight part -- usually -- 1 - 99 weight part -- desirable -- 5 - 70 weight part -- it is 10 - 40 weight part more preferably.

[0027] Screw amide compounds can be blended with the constituent of polyamide resin (X) in order to raise the slide nature on the surface of a film. Specifically as screw amide compounds, N and N'- methylene-bis-stearylamine, N, N'-ethylene-bis-stearylamine etc. is mentioned. The amount of addition of screw amide compounds is 0.01 - 1 weight part preferably to a polyamide resin 100 weight part, and is a 0.01 - 0.3 weight part especially preferably.

[0028] Various kinds of resin additive agents, such as lubricant, a release agent, a heat deterioration prevention agent, an ultraviolet ray absorbent, a spray for preventing static electricity, an antiblocking agent, dye, paints, fire retardant, and a spreading agent, can be blended with the constituent of polyamide resin (X) in the kind and range which do not spoil the purpose of this invention.

[0029] As a method of blending an antioxidant, a filler with an average particle diameter of 10 micrometers or less and a screw amide compound, and other additive agents with polyamide resin (X) [, / carry out a dry blend to polyamide resin after carrying out heavy condensation, or] [adding in the heavy condensation process of polyamide resin] The method known from the former is mentioned, such as carrying out fusion kneading with polyamide resin, or producing a high-concentration master batch, diluting this at the time of fabrication, and blending with polyamide resin.

[0030] In order to prepare a packing object from the lamination film concerning this invention, the layer made of the thermoplastics (Z) of the range of 100 degrees C - 170 degrees C of melting points is arranged to the innermost layer of a packing object. It functions as a thermoplastics (Z) layer raising the heat-sealing nature at the time of preparing a packing object from a lamination film while raising the intensity of a lamination film. Preferably, since it fuses when the melting point of thermoplastics (Z) carries out pneumaticity retorting at less than 100 degrees C, if it exceeds 170 degrees C, heat-sealing intensity runs short and it is not desirable on manufacture of a packing object. In addition, the melting point can be measured by the DSC method etc.

[0031] As an example of the thermoplastics (Z) of 170 degrees C or less of melting points, polypropylene, polyethylene, a polypropylene copolymer, etc. are mentioned preferably. As a polypropylene copolymer, a copolymer with propylene, ethylene, 1-BUTEN, etc. is mentioned. At least one sort of these thermoplastics (Z) may be two or more sorts of mixtures.

[0032] The adhesive resin layer (Y) which constitutes the lamination film concerning this invention functions as pasting up firmly the border plane of a polyamide resin (X) layer and a thermoplastics (Z) layer. As an adhesive resin layer (Y), denaturation polyolefin resin is

suitable. Denaturation polyolefin resin says the polyolefin resin which denatured with alpha and beta-unsaturated carboxylic acid. OREFIN which specifically use ethylene and propylene as a main composition ingredient The graft polymerization thing (b) which carried out the graft of alpha and beta-unsaturated carboxylic acid or its derivative to the polymerization thing of OREFIN which uses alpha and beta-unsaturated carboxylic acid or the copolymerization thing (a) of the derivative and ethylene, and propylene as a main composition ingredient is mentioned.

[0033] As alpha in the above-mentioned copolymerization thing (a), beta-unsaturated carboxylic acid, or its derivative, acrylic acid, methacrylic acid, MECHIRU methacrylic acid, acrylic acid sodium, acrylic acid zinc, acetic acid vinyl, glycidyl methacrylate, etc. are mentioned, for example. as the example of a copolymerization thing (a) -- an ethylene-vinyl acetate copolymer, an ethylene acrylic acid copolymer, an ethylene ethyl acrylic acid copolymer, an ethylene acrylic acid sodium copolymer, etc. -- etc. -- *****. The rate of alpha in the above-mentioned copolymerization thing (a), beta-unsaturated carboxylic acid, or its derivative is less than 40 mol % preferably.

[0034] As a polymerization thing of OREFIN used as the foundations of a graft polymerization thing (b) For example, polyethylene, polypropylene, an ethylene propylene copolymer, An ethylene butene-1 copolymer, an ethylene-vinyl acetate copolymer, an ethylene acrylic acid copolymer, an ethylene ethyl acrylic acid copolymer, an ethylene acrylic acid sodium copolymer, etc. are mentioned.

[0035] As alpha by which a graft is carried out to the polymerization thing of above-mentioned OREFIN, beta-unsaturated carboxylic acid, or its derivative, ester, such as acrylic acid, meta-acrylic acid, Etah Kurile acid, maleic acid, fumaric acid, these acid anhydrides, these acid, and tetrahydrofurfuryl alcohol, is mentioned. A desirable ingredient by which a graft is carried out is a maleic anhydride. The amount of grafts to the polymerization thing of OREFIN is 0.05 to 1.5weight % of an olefin polymerization thing preferably.

[0036] In order to carry out the graft of alpha and beta-unsaturated carboxylic acid or its derivative to the polymerization thing of OREFIN, both ingredients are mixed according to a usual state method, and it is carried out by making it fuse with the resin temperature of 150-300 degrees C. Graft polymerization is efficiently executable if alpha and organic peroxide like alpha-****- tert-butyl peroxide p-diisopropylbenzene are blended 0.001 to 0.05weight % to the polymerization thing of OREFIN on the occasion of graft polymerization.

[0037] To the above-mentioned denaturation polyolefin resin, non-denatured polyolefin resin is mixable in 0 to 90weight % of the range. Adhesiveness falls and is not desirable if non-denatured polyolefin resin becomes 90weight % or more. It is the range which does not spoil the purpose of this invention, and various kinds of resin additive agents currently used from the former, such as paints, dye, heat stabilizer, and a spray for preventing static electricity, can be

further blended with denaturation polyolefin resin.

[0038] The lamination film concerning this invention, for example (1) co-extrusion sheet forming, co-extrusion T Di fabrication, What is called the co-extruding methods, such as co-extrusion air cooling inflation fabrication and co-extrusion water-cooled inflation fabrication, (2) After manufacturing extension or a non-extended monolayer film, it can manufacture by the method of laminating with other films by the lamination nation method, the method of carrying out extension fabrication of the (3) lamination film, and manufacturing a lamination oriented film, etc. As the extension method of a monolayer film or a lamination film, it can be based on the extension method known from the former, and the tubular type or tenter type simultaneous biaxial extending method, the serial biaxial extending method which carries out tenter type horizontal extension after roll type length extension, etc. are specifically mentioned.

[0039] The thickness of the lamination film concerning this invention is chosen in 3-300 micrometers. If the thickness of a lamination film is too thick, transparency will fall, if too thin, pinhole-proof nature will fall easily, and neither is desirable. Let the ratio of the thickness of each layer which constitutes a lamination film be a polyamide resin (X) layer 90 - 10% and an adhesive resin (Y) layer 1 - layer [50% and 10 to 90% of (Z) thermoplastics (Z) layer] ratio. If it shifts from this ratio range, intensity degradation of the film after carrying out pneumaticity retorting is remarkable, or heat-sealing nature does not have it. [bad desirable] The lamination film concerning this invention can also perform corona discharge treatment to one side or both sides for the purpose of improvement of printing nature, and improvement of lamination nature.

[0040] Although the lamination film concerning this invention contains three layers, a polyamide resin (X) layer, an adhesive resin (Y) layer, and a thermoplastics (Z) layer, it can also laminate the film and aluminum foil made of thermoplastics of further others. As a film made of other thermoplastics, polyamide resin other than polyamide resin (X), Half-aromatic polyamide resin, an ethylene vinyl alcohol copolymer, a polyvinylidene chloride, polyethylene, polypropylene, an ethylene-vinyl acetate copolymer, polyester resin, etc. are mentioned. Between the above-mentioned (X) layer and the (Y) layer, the form at the time of laminating other films and aluminum foil made of thermoplastics can be arranged between the (Y) layer and the (Z) layer etc., or can be arranged on the surface of (X) layer. Under the present circumstances, as for the border plane of a layer and a layer, it is desirable to make the (Y) layer intervene.

[0041] The lamination film concerning this invention has that desirable whose intensity maintenance rate after [30 minutes] carrying out pneumaticity retorting is 60% or more at 130 degrees C about a lamination film. That an intensity maintenance rate is 60% or more means being hard to produce strength reduction, even if it carries out pneumaticity retorting, and it can be attained for the purpose of this invention. On the other hand, if pneumaticity retorting is

carried out to an intensity maintenance rate being less than 60%, it means being easy to produce strength reduction, and the purpose of this invention cannot be attained.

[0042] The packing object concerning the 2nd invention of this invention can be manufactured using the lamination film concerning the 1st above-mentioned invention. The method in particular of manufacturing the packing object concerning the 2nd invention is not limited, can make the (Z) layer or the film layer made of other thermoplastics excellent in heat-sealing nature able to counter as an innermost layer, and can be based on the method of heat sealing. [turn / the form of heat sealing / the innermost layer of a lamination film] Pile up the two sheets and further the peripheral edge of the perimeter, for example Or a side seal type, they are the method seal type of two, the method seal type of three, the method seal type of four, a *****RISHIRU type, a *****RISHIRU type (pillow seal type), and ** -- it is attached and the method of carrying out a seal mentions according to heat-sealing forms, such as a seal type, a flat bottom seal type, and a square bottom seal type, etc. -- ****. A tube container can be manufactured using the lamination film concerning the 1st invention.

[0043] The method in particular of the above-mentioned heat sealing is not limited, and can be based on methods known from the former, such as the bar seal method, the rotation roll seal method, the belt seal method, the impulse seal method, the high frequency seal method, and the ultrasonic seal method. Bung holes, such as a dress type and a two-piece type, the zipper for opening and closing, etc. can also be attached to the packing object acquired by the above-mentioned seal method.

[0044] The lamination film concerning the 1st invention of this invention is applicable to manufacture of the packing object concerning the 2nd invention of this invention. After the packing object concerning the 2nd invention stores goods, it is preferably used as a container for storage of the medical supply by which germicidal treatment is carried out at high temperature etc. before goods storage besides the container for storage of the various food by which pneumaticity retorting is carried out. The form in particular of a packing object is not restricted.

[0045]

[Example] Hereafter, although a work example explains this invention still in detail, this invention is not limited to the following work examples, unless the summary is exceeded. In addition, the materials used by the following work examples and comparative examples are as follows.

[0046] (1) PA1-PA8 (polyamide resin)

A churning machine, a thermometer, a reflux condenser, a jacket, etc. It is ***** which showed amine and carboxylic acid of caprolactam 60kg, 0.1l. of 5% solution of phosphorous acid hydrogen disodium, and the kind shown table-1 to the autoclave with a capacity of 200l. equipped table-1, respectively. Agitating at 16rpm, after carrying out nitrogen substitution of

these with an autoclave sealed, it pushed and heated in the heat carrier in the jacket, and the condensation reaction was performed. When the internal temperature of 270 degrees C and gage pressure 0.8MPa reached, pressure was discharged to atmospheric pressure, and it decompressed gradually until it became the shown last pressure subsequently to table-1. [0047] After reaching predetermined pressure, the reaction was performed for further 3 hours. Then, after having stopped churning, introducing nitrogen and returning to normal pressure, from the autoclave, obtained polyamide was made into the shape of Strand, and was extracted, and it cut and pelletized by the revolving cutter. Operation of having supplied the obtained pellet to 150l. of boil pure water, and extracting an unreacted monomer was repeated 5 times. It dried after the end of extraction operation until the amount of moisture became 0.1% or less by 120 degrees C and 0.1kPa, and eight kinds of polyamide resin (PA1-PA8) was obtained. In addition, PA4 were dried, without carrying out extraction operation by boil pure water.

[0048]

[Table 1]

表-1

項目 番号	変性成分				最終圧力 (kpa)	抽出操作
	アミンの 種類	アミンの 添加量	カルボン酸 の種類	カルボン酸 の添加量		
PA1	HMDA	63	なし	—	16	あり
PA2	HMDA	43	なし	—	25	あり
PA3	HMDA	30	なし	—	24	あり
PA4	HMDA	63	なし	—	16	なし
PA5	なし	—	なし	—	38	あり
PA6	HMDA	40	S t 酸	40	8	あり
PA7	なし	—	酢 酸	30	37	あり
PA8	ODA	5	S t 酸	5	29	あり

[注]

- (1) 変性成分添加量の単位は、 $\mu\text{eq}/\text{樹脂}1\text{ g}$ である。
- (2) HMDAは、ヘキサメチレンジアミンを意味する。
- (3) ODAは、オクタデシルアミンを意味する。
- (4) S t 酸は、ステアリン酸を意味する。

[0049] The amount of end amino groups of eight kinds of polyamide resin (PA1-PA8), the amount of end carboxyl groups, relative viscosity, the amount of water extraction, etc. were made a fixed quantity by the above mentioned method. The result was shown in table-2. The melting point of **** and polyamide resin PA1 was 221 degrees C.

[0050]

[Table 2]

表-2

項目 番号	(B)	(A)	(C)	相対粘度	水抽出量 (重量%)
PA1	72	7	65	3.2	0.6
PA2	58	14	44	3.6	0.6
PA3	46	16	30	4.4	0.6
PA4	72	7	65	3.2	4.0
PA5	35	35	0	3.7	0.6
PA6	17	13	4	3.6	0.6
PA7	23	52	-29	3.3	0.6
PA8	31	30	1	3.6	0.6

[注]

(A) は、ポリアミド樹脂の末端カルボキシル基量(meq/
樹脂1g)を意味する。

(B) は、ポリアミド樹脂の末端アミノ基量(meq/樹脂
1g)を意味する。

(C) は、(B) - (A) を意味する。

[0051] (2) AO1:N and N'-HEKISA methylene screw (3, 5-G t-butyl 4-hydroxy hydronalium thinner MAMIDO) (the Ciba-Geigy make, antioxidants, a brand name: IRUGANOKKUSU 1098).

(3) AO2 : pentaerythrityl tetrakis {3-(3, 5-G t-butyl 4-hydroxyphenyl) propionate} (the Ciba-Geigy make, antioxidants, a brand name: IRUGANOKKUSU 1010).

[0052] (4) F1 : silica of the average particle diameter of 1.5 micrometers, and a refractive index 1.46 (the Fuji SHIRISHIA chemistry company make, a brand name: SAIRISHIA 310).

(5) F2 : zeolite of the average particle diameter of 5.5 micrometers, and a refractive index 1.5 (Mizusawa Industrial Chemicals, Ltd. make and brand name:SHIRUTONAMT50).

(6) F3 : bridge construction PMMA of the average particle diameter of 6.0 micrometers, and a refractive index 1.5 (the NIPPON SHOKUBAI [Co., Ltd.] make, a brand name: EPO star MA1006).

[0053] (7) AD1 : polyolefin system adhesiveness resin (the Mitsubishi Chemical make, a brand name: Modic AP and grade name:P513V).

(8) PO1 : the polypropylene copolymer of 170 degrees C or less of melting points (Japan Polychem make and grade name:EG7C).

[0054] The evaluation test of the lamination film and the packing object was done on the following by the method of the description.

(a) Film production nature : three-layer inflation film production machine (made by Placo) [the three layer film which consists of (X) layer (140 micrometers in thickness), a (Y) layer (10 micrometers in thickness), and a (Z) layer (30 micrometers in thickness)] The 180-micrometer-thick lamination film was manufactured by the water-cooled inflation method, and visual observation of the existence of the die line generated on a three-layer film in this case, the existence of a fish eye, etc. was carried out. What these are not accepted in was judged to be

O, what is accepted was judged to be x, and it displayed.

[0055] (b) Breaking strength : the temperature of 23 degrees C and 65% of humidity are under the conditions of RH about the lamination film of a sample, As for the film which does not carry out pneumaticity retorting, it will tone-** four days or more, the tensilon by an ORIEN tech company is used, and the film after one day and pneumaticity retorting is JIS. **** breaking strength was evaluated according to K7127. The intensity maintenance rate (%) was computed according to the following formula, i.e., (the breaking strength of the film after pneumaticity retorting) / (breaking strength of the film which does not carry out pneumaticity retorting) x100. An intensity maintenance rate is so desirable that a numerical value is large at 60% or more. If lower than this, it will be easy to damage a packing bag after pneumaticity retorting.

[0056] In addition, the pneumaticity retorting method about a lamination film was carried out as follows. A lamination film is cut to the specimen of the size of 160mm of the directions of direction of MD 280 mmxTD, and it fixes to the ** implement made from stainless steel. the autoclave for pneumaticity retorting of a pouch-packed food (Tommy elaborate company make --) Form :SR-It put into 240 types, when ****(ed) to 100 degrees C, the exhaust valve was closed after that, **** and ** pressure were continued and the internal temperature amounted to 130 degrees C, discharging the air in an autoclave first, pressurization with air was performed, and internal pressure was set to 0.31Mpa and held for 30 minutes. Internal pressure was pressurized after that at 0.34Mpa, cooling water was put into the autoclave, and the internal temperature was cooled to 70 degrees C. the bottom of the temperature of 23 degrees C after removing the film after cooling from a ***** implement and wiping off moisture, and 65%RH -- ***** -- **** breaking strength was measured.

[0057] (c) Heat-sealing nature : cut a lamination film to the specimen of the size of 160mm of the directions of direction of MD 400 mmxTD, make the direction of MD into the length of a long side which it bends in the center mostly and is a half that a inner layer seems to become inside, and it is the impulse seal method at 170 degrees C about a both-sides end. It heat sealed and the packing object (200mm x 160mm) was manufactured. Under the present circumstances, the thing in which O and heat sealing were impossible was displayed for what was able to be heat sealed as x.

[0058] (d) After-retorting drop test : 200g of water which colored the packing object manufactured by the above-mentioned heat-sealing nature examination was put in, and the packing object which heat sealed the remaining ends and enclosed water was prepared, deaerating the packing inside of the body. After putting the packing object which enclosed the obtained water into the above-mentioned autoclave for pneumaticity retorting and carrying out pneumaticity retorting for 30 minutes at the temperature of 130 degrees C with the same procedure as the above, the packing object which enclosed water was dropped from a height of 50cm to the floor, and visual observation of the existence of disclosure of a content was

carried out. or [that O and disclosure were accepted in what disclosure was not accepted in from the packing object which enclosed water] -- or what carried out bag tearing was displayed as x.

[0059] [A work example 1 - a work example 6 and a comparative example 1 - comparative example 5] [the above PA1-PA8 {polyamide resin (X)}] A filler is blended for the antioxidant of the kind shown in table-2, and quantity, respectively, and it is a three-layer inflation film production machine (made by Placo) about three sorts of resin of AD1 {adhesive resin (Y)} and PO1 {thermoplastics (Z)}. The three-layer film whose thickness of the whole which consists of (X) layer (140 micrometers in thickness), a (Y) layer (10 micrometers in thickness), and a (Z) layer (30 micrometers in thickness) is 180 micrometers was manufactured by the water-cooled inflation method. Film production nature was evaluated at the time of manufacture of a lamination film. Then, with the biaxial drawing machine (made by TM long company), the simultaneous biaxial drawing of the draw ratio was increased 3x3 times at the temperature of 80 degrees C, the heat set of this lamination film was carried out at the temperature of 210 degrees C, and the 20-micrometer-thick lamination oriented film made of polyamide resin was manufactured. Breaking strength was measured about the obtained lamination oriented film. The measurement result was shown in table-3.

[0060]

[Table 3]

表-3

項目 番号	種 類	ポリアミド樹脂 (X)				製膜性	破 断 強 度		
		酸化防止剤		フィラー			引伸率 理前	引伸率 理後	保持率 (%)
		種 類	添加量	種類	添加量				
実施例 1	PA1	—	—	—	—	○	260	200	77
実施例 2	PA2	—	—	—	—	○	245	175	71
実施例 3	PA3	—	—	—	—	○	255	180	71
実施例 4	PA3	AO1	0.1	—	—	○	285	195	74
実施例 5	PA1	AO2	0.05	—	—	○	270	220	81
実施例 6	PA1	AO1	0.03	F1	0.1	○	200	150	75
比較例 1	PA5	—	—	—	—	○	200	35	18
比較例 2	PA6	AO1	0.03	—	—	○	220	100	45
比較例 3	PA7	AO1	0.03	—	—	○	150	50	33
比較例 4	PA8	—	—	—	—	○	210	40	19
比較例 5	PA4	—	—	—	—	×	—	—	—

[0061] Table -The following thing becomes clear from 1 to table-3.

(1) the lamination film of the work example of this invention -- the difference of the amount of end groups of polyamide resin (X) -- since (C {amount of (amount B) of end amino groups-end carboxyl groups (A)}), relative viscosity, the amount of water extraction, etc. are made into the range specified by Claim 1 Even if the intensity maintenance rate after pneumaticity retorting is higher than 60% and carries out pneumaticity retorting, intensity does not fall sharply (refer to

a work example 1 - a work example 6).

(2) When an antioxidant is blended with polyamide resin (X), compared with the case where this is not blended, the strength reduction after carrying out pneumaticity retorting is small (refer to a work example 1, a work example 5 and a work example 3, and a work example 5).

(3) On the other hand, the lamination film of less than ten comparative example has [the difference (C) of the amount of end groups of polyamide resin (X)] an intensity maintenance rate lower than 60% after pneumaticity retorting, and intensity falls sharply by pneumaticity retorting (refer to a comparative example 1 - a comparative example 4).

(4) Since a lot of gas occurred during film production, many die lines and fish eyes occurred on the film and the thing of the comparative example 5 for which the amount of water extraction used 2weight % or more of PA4 was inferior in appearance further, measurement of breaking strength was not performed.

[0062] [A work example 7 - a work example 13 and a comparative example 6 - comparative example 7] [Above PA {polyamide resin (X)}] A filler is blended for the antioxidant of the kind shown in table-3, and quantity, respectively, and it is a three-layer inflation film production machine (made by Placo) about three sorts of resin of AD1 {adhesive resin (Y)} and PO1 {thermoplastics (Z)}. The three-layer film whose thickness of the whole which consists of (X) layer (40 micrometers in thickness), a (Y) layer (3 micrometers in thickness), and a (Z) layer (7 micrometers in thickness) is 50 micrometers was manufactured by the water-cooled inflation method. About the obtained lamination film, breaking strength was measured and the measurement result was shown in table-4.

[0063]

[Table 4]

表-4

項目 番号	ポリアミド樹脂 (X)						破 断 強 度		
	種 類		添加量		フィラー		引伸率		保持率 (%)
	種 類	種 類	種 類	種 類	種 類	種 類	理前	理後	
実施例 7	PA1	—	—	—	—	—	105	90	86
実施例 8	PA2	—	—	—	—	—	110	100	91
実施例 9	PA3	—	—	—	—	—	100	85	85
実施例10	PA3	AO1	0.1	—	—	—	105	95	90
実施例11	PA1	AO2	0.05	—	—	—	105	95	90
実施例12	PA1	AO1	0.03	F2	0.2	—	100	85	85
実施例13	PA1	AO1	0.03	F3	0.1	—	100	85	85
比較例 6	PA5	—	—	—	—	—	100	40	40
比較例 7	PA5	AO1	0.03	—	—	—	100	50	50

[0064] Table -The following thing becomes clear from 1, table-2, and table-4.

(1) the lamination film of the work example of this invention -- the difference of the amount of end groups of polyamide resin (X) -- since (C {amount of (amount B) of end amino groups-end carboxyl groups (A)}), relative viscosity, the amount of water extraction, etc. are made into the

range specified by Claim 1 Even if the intensity maintenance rate after pneumaticity retorting is higher than 60% and carries out pneumaticity retorting, intensity does not fall sharply (refer to a work example 7 - a work example 13).

(2) When an antioxidant is blended with polyamide resin (X), compared with the case where this is not blended, the strength reduction after carrying out pneumaticity retorting is small (refer to a work example 9, a work example 10 and a work example 7, and a work example 11).

(3) On the other hand, the lamination film of less than ten comparative example has [the difference (C) of the amount of end groups of polyamide resin (X)] an intensity maintenance rate lower than 60% after pneumaticity retorting, and intensity falls sharply by pneumaticity retorting (refer to a comparative example 6 - a comparative example 7).

[0065] [A work example 14 - a work example 15 and a comparative example 8 - comparative example 9] [Above PA {polyamide resin (X)}] A filler is blended for the antioxidant of the kind shown in table-4, and quantity, respectively, and it is a three-layer inflation film production machine (made by Placo) about AD1 {adhesive resin (Y)} and three sorts of resin of thermoplastics (Z). The 50-micrometer-thick lamination film [film / which consists of (X) layer (40 micrometers in thickness), a (Y) layer (3 micrometers in thickness), and a (Z) layer (7 micrometers in thickness) / three layer / method / water-cooled inflation] was manufactured. About the obtained lamination film, breaking strength was measured and the measurement result was shown in table-5.

[0066]

[Table 5]

表-5

項目 番号	ポリアミド樹脂 (X)				熱可塑性 樹脂 (Z) の種類	ヒート シール 性	レトルト 処理後 落下試験
	種 類	酸化防止剤 種 類	添加量	フィラー 種類	添加量		
実施例14	PA1	—	—	—	—	PO1	○
実施例15	PA3	AO1	0.1	—	—	PO1	○
比較例8	PA5	—	—	—	—	PO1	○
比較例9	PA1	—	—	—	—	PA1	×

[0067] Table -The following thing becomes clear from 1, table-2, and table-5.

(1) That from which the lamination film of the work example of this invention constituted the innermost layer with polyolefin system resin is excellent in heat-sealing nature, and even if seal intensity is strong, and it does the drop test of a packing object after retorting, it is hard to damage it (refer to a work example 14 - a work example 15).

(2) On the other hand, even if polyolefin system resin constitutes an innermost layer, although the packing object of less than ten comparative example 8 excels [nature / heat-sealing] in the difference (C) of the amount of end groups of polyamide resin (X), damage by the drop test

of a packing object after retorting, and seal intensity is weak. Moreover, the comparative example 9 which used the innermost layer as polyamide resin is also inferior to heat-sealing nature, and cannot be processed into a packing object.

[0068]

[Effect of the Invention] this invention is as having explained to details above, and is as follows -- doing an advantageous effect so specially, the industrial utility value is size very much.

1. Lamination Film Concerning this Invention -- Difference of the Amount of End Groups of Polyamide Resin (X) -- since (C {Amount of (Amount B) of End Amino Groups-End Carboxyl Groups (A)}), Relative Viscosity, the Amount of Water Extraction, Etc. are Made into Specific Range Even if the intensity maintenance rate after pneumaticity retorting is higher than 60% and carries out pneumaticity retorting, intensity does not fall sharply. Therefore, it is suitable as an object for packing object manufacture of the various food by which RETORRUTO processing is carried out.

2. since the amount of water extraction of polyamide resin (X) is made into the specific range, the lamination film concerning this invention has little quantity of the gas which occurs at the time of film manufacture, and neither a die line nor a fish eye generates it easily -- appearance -- excellent -- **** .

3. The lamination film concerning this invention improves and has a desirable intensity maintenance rate after pneumaticity retorting, when an antioxidant is blended with polyamide resin (X).

4. Since the intensity maintenance rate after [30 minutes] carrying out pneumaticity retorting is 60% or more at 130 degrees C, even if the lamination film concerning this invention falls after processing it into a packing object and retorting it, it is suitable as an object for storage of the various food which are RETORRUTO-processing-made hard to damage.

5. Since the packing object prepared from the lamination film concerning this invention constitutes the innermost layer with polyolefin system resin, it is excellent in heat-sealing nature, and excellent also in seal intensity.

[Translation done.]